

Electronic supporting information

High current density electrodeposition of silver from silver-
containing liquid metal salts with pyridine-*N*-oxide ligands

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Table S1: Selected bond lengths and interatomic distances in the crystal structures of α -[Ag(py-O)₃][Tf₂N], β -[Ag(py-O)₃][Tf₂N], [Ag₃(py-O)₈][OTf]₃, [Ag(py-O)₂][OMs] and [Ag(py-O)₂][NO₃].

Compound	Ag-O	Distance (Å)	Ag-Ag	Distance (Å)	Compound	Ag-O	Distance (Å)	Ag-Ag	Distance (Å)
α -[Ag(py-O) ₃][Tf ₂ N]	Ag1 - O7	2.455(4)	Ag1 - Ag2	3.247(1)	[Ag ₃ (py-O) ₈][OTf] ₃	Ag1 - O1	2.271(3)	Ag1 - Ag2	3.2915(5)
	Ag1 - O8	2.490(4)	Ag2 - Ag3	3.1054(8)		Ag1 - O8	2.599(3)	Ag2 - Ag3	3.3210(5)
	Ag2 - O8	2.444(4)	Ag3 - Ag4	3.2004(8)		Ag1 - O15	2.477(3)		
	Ag2 - O9	2.489(3)	Ag4 - Ag1	3.0244(7)		Ag1 - O22	2.459(3)		
	Ag3 - O9	2.494(3)	Ag5 - Ag6	3.2300(8)		Ag1 - O29	2.409(3)		
	Ag3 - O10	2.449(3)	Ag5 - Ag6	3.0586(8)		Ag2 - O8	2.478(3)		
	Ag4 - O7	2.527(4)				Ag2 - O15	2.559(3)		
	Ag4 - O10	2.451(3)				Ag2 - O22	2.448(3)		
	Ag5 - O11	2.463(3)				Ag2 - O43	2.413(3)		
	Ag5 - O12	2.499(3)				Ag2 - O36	2.488(3)		
	Ag6 - O11	2.461(3)				Ag2 - O43	2.413(3)		
	Ag6 - O12	2.491(3)				Ag3 - O15	2.444(3)		
β -[Ag(py-O) ₃][Tf ₂ N]	Ag1 - O1	2.4842(2)	Ag1 - Ag2	3.1508(3)		Ag3 - O29	2.556(4)		
	Ag2 - O1	2.4722(2)	Ag2 - Ag3	3.1598(4)		Ag3 - O36	2.333(3)		
	Ag2 - O2	2.4905(2)	Ag3 - Ag4	3.2238(4)		Ag3 - O43	2.632(3)		
	Ag3 - O2	2.4748(2)	Ag4 - Ag5	3.0803(4)		Ag3 - O50	2.248(3)		
	Ag3 - O3	2.4665(2)	Ag5 - Ag6	3.0522(4)	[Ag(py-O) ₃][OTf]	Ag1 - O2	2.4621(1)	Ag1 - Ag1	3.0191(2)
	Ag4 - O3	2.4490(2)	Ag6 - Ag7	3.1935(4)		Ag1 - O2	2.5117(1)		
	Ag4 - O4	2.4918(2)	Ag7 - Ag8	3.1039(4)		Ag1 - O3	2.3651(1)		
	Ag5 - O4	2.4806(2)	Ag8 - Ag9	3.0418(4)		Ag1 - O4	2.3957(1)		
	Ag5 - O5	2.513(2)	Ag9 - Ag10	3.2032(3)		Ag1 - O4i	2.4892(1)		
	Ag6 - O5	2.490(2)	Ag10 - Ag9	3.2036(3)	[Ag(py-O) ₂][OMs]	Ag1 - O2	2.4108(2)		
	Ag6 - O6	2.4587(2)				Ag1 - O3	2.3386(1)		
	Ag7 - O6	2.4762(2)				Ag1 - O3	2.3430(1)		
	Ag7 - O7	2.4898(2)				Ag1 - O4	2.4961(1)		
	Ag8 - O7	2.4893(2)				Ag1 - O4	2.5828(1)		
	Ag8 - O8	2.4799(2)			[Ag(py-O) ₂][NO ₃]	Ag1 - O2	2.5225(1)		
	Ag9 - O8	2.4900(2)				Ag1 - O2	2.3228(1)		
	Ag9 - O9	2.4664(2)				Ag1 - O3	2.2958(1)		
	Ag10 - O9	2.4698(2)				Ag1 - O4	2.5193(1)		
						Ag1 - O5	2.4253(1)		

Table S2: π - π interactions for the different compounds. The lettering of the planes is presented in the respective figures of the compounds.

Compound	Planes	Angle (°)	centroid-centroid distance (Å)	shift (Å)
α -[Ag(py-O) ₃][Tf ₂ N]	A-B ⁱ	4.3	3.608	1.474
β -[Ag(py-O) ₃][Tf ₂ N]	A-Q ⁱⁱ	4.0	3.714	1.753
	B-C ⁱⁱⁱ	8.0	3.583	1.121
	E-F ^{iv}	4.8	3.788	2.052
	F-G ^v	2.5	3.649	1.580
	G-H ^{vi}	5.0	3.891	2.101
	I-J ^{vii}	1.9	3.870	1.923
	J-K ^{viii}	3.7	3.668	1.621
	K-L ^{ix}	5.0	3.802	1.879
	N-O ^x	9.2	3.575	1.459
[Ag ₃ (py-O) ₈][OTf] ₃	A-B ^{xi}	6.3	3.883	2.219
	C-F ^{xii}	3.1	3.606	1.071
	C-F ^{xiii}	3.1	3.778	1.911
	D-G ^{xiv}	9.4	3.503	0.940
	D-G _i ^{xv}	9.4	3.715	1.228
	E-H ^{xvi}	2.6	3.693	1.598
[Ag(py-O) ₃][OTf]	A-C ^{xvii}	15.7	3.799	1.797
	B-C ^{xviii}	13.8	3.714	0.812
[Ag(py-O) ₂][OMs]	A-A ^{xix}	0	3.804	1.969
	A-B ^{xx}	9.0	3.533	0.995
[Ag(py-O) ₂][NO ₃]	A-B ^{xxi}	2.8	3.668	1.671
Symmetry operations:				
<i>i</i>	1-x, +x-y, +z		<i>xiii</i>	+x, +y, +z
<i>ii</i>	+y-x, 1-x, 1+z		<i>xiv</i>	-1+x, +y, +z
<i>iii</i>	+x, +y, +z		<i>xv</i>	+x, +y, +z
<i>iv</i>	+x, +y, +z		<i>xvi</i>	+x, +y, +z
<i>v</i>	+x, +y, +z		<i>xvii</i>	3/4-y, 1/4+x, 1/4+z
<i>vi</i>	+y-x, 1-x, +z		<i>xviii</i>	-1/4+y, 3/4-x, -1/4+z
<i>vii</i>	+y-x, 1-x, +z		<i>xix</i>	2-x, 2-y, -z
<i>viii</i>	1-y, 1+x, +z		<i>xx</i>	+x, +y, +z
<i>ix</i>	+y-x, 1-x, +z		<i>xxi</i>	-x, 1-y, 1-z
<i>x</i>	+x, +y, +z			
<i>xi</i>	+x, +y, +z			
<i>xii</i>	-1+x, +y, +z			

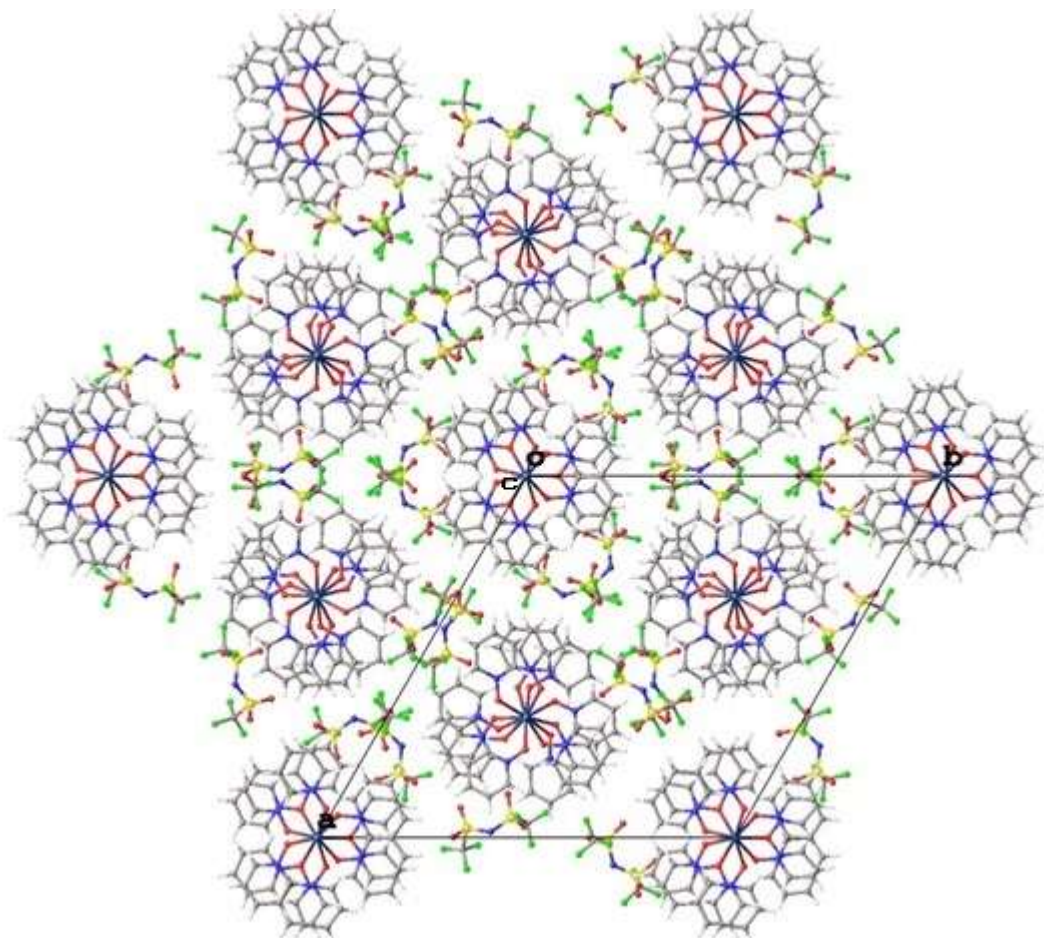


Figure S1: View along the c axis of the packing in the crystal structure of α -[Ag(py-O)₃][Tf₂N] showing the two different [Ag(py-O)₃]_∞ chains with the bis(trifluoromethanesulfonyl)imide anions in between. Disorder of the anions is omitted for clarity.

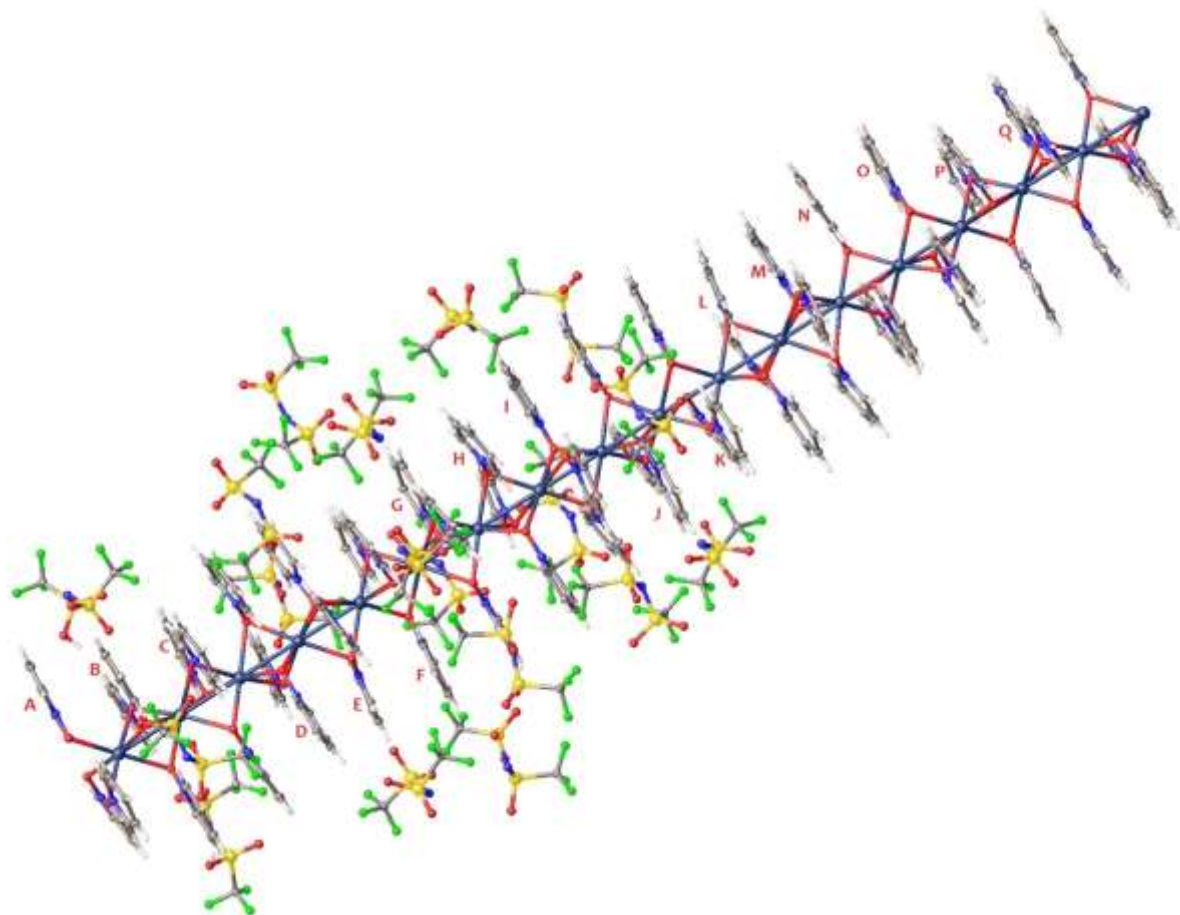


Figure S2: View of the crystal structure of β -[Ag(py-O)₃][Tf₂N] showing the Ag...Ag interactions. Disorder of the anions is omitted for clarity.

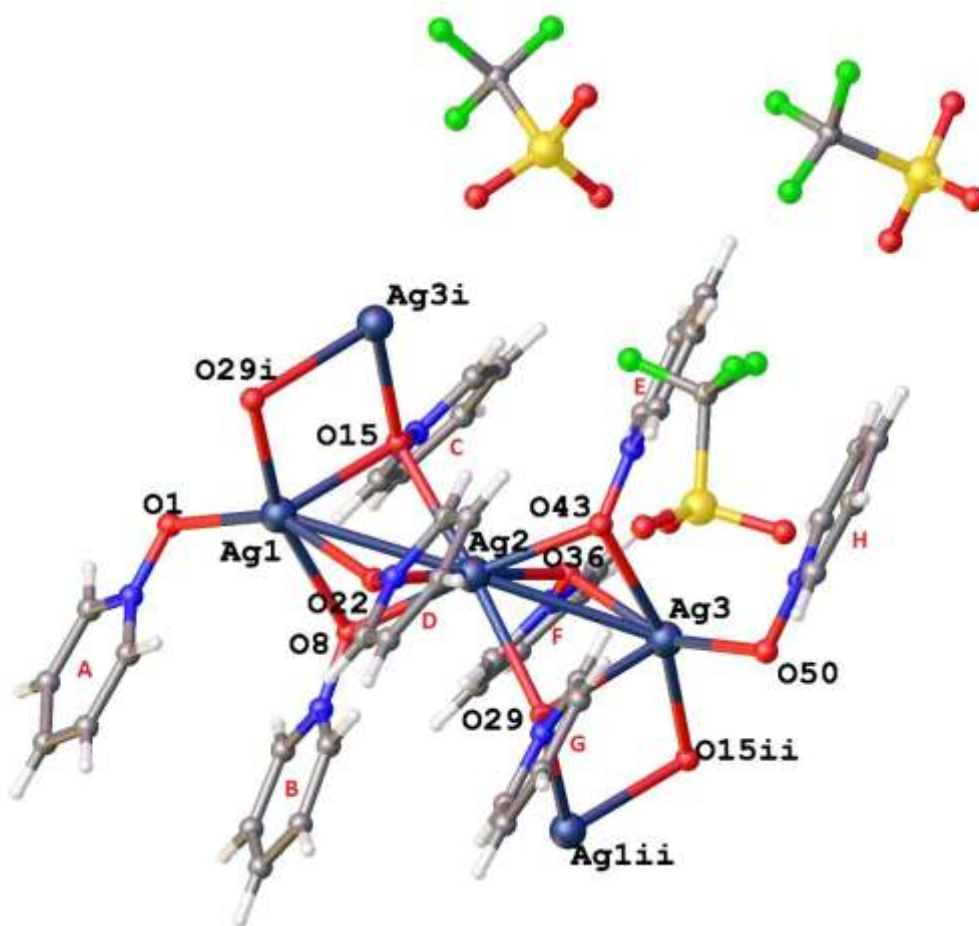


Figure S3: View of the crystal structure of $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$ showing the coordination environment of the silver centres and the bridging nature of the py-O ligands. (symmetry codes: i 1-x, y, z; ii 1+x, y, z).

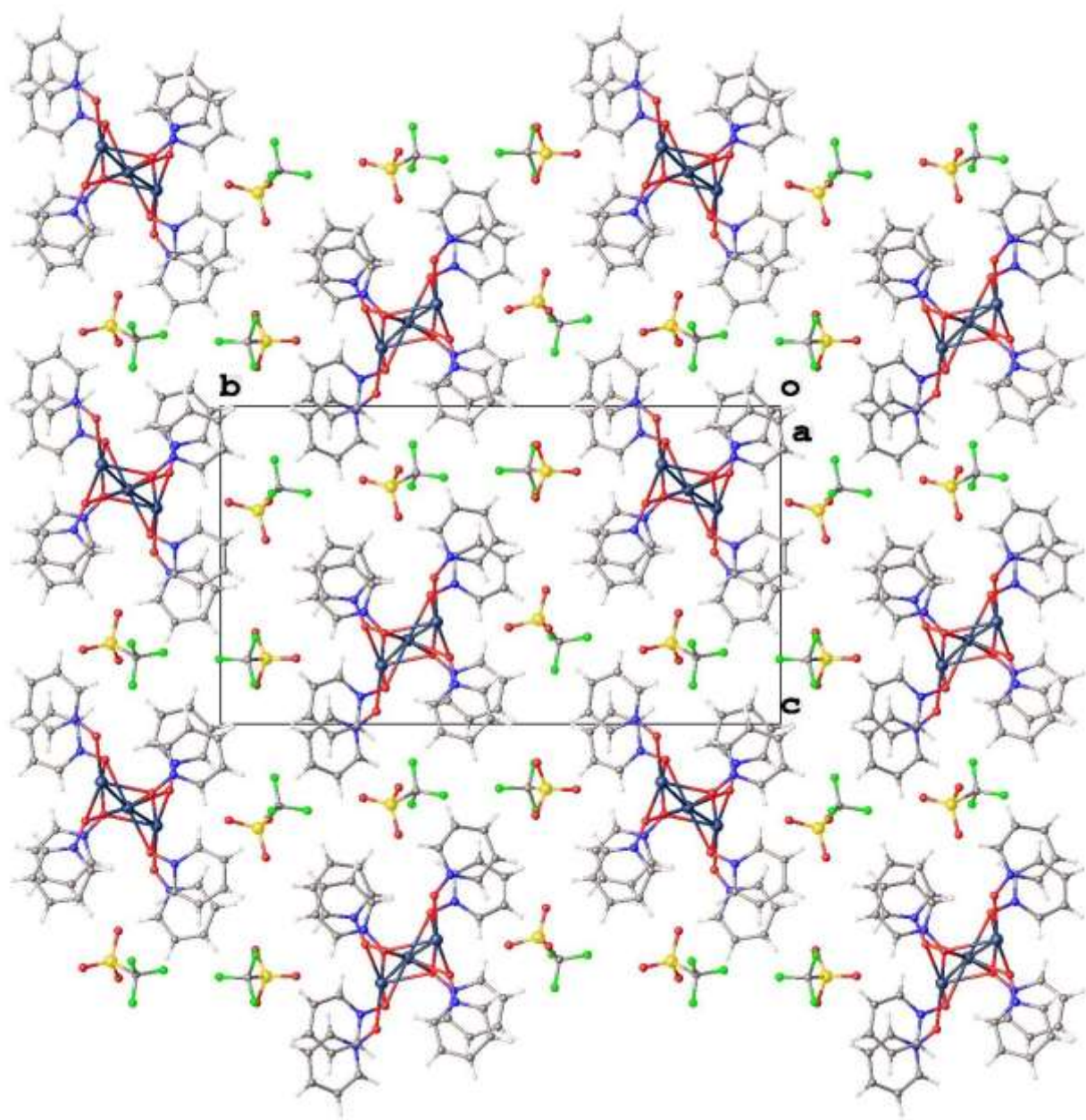


Figure S4: View of the packing in the crystal structure of $[\text{Ag}_3(\text{py-O})_8][\text{OTf}]_3$ showing the π - π interactions and the packing of the chains and uncoordinated OTf anions.

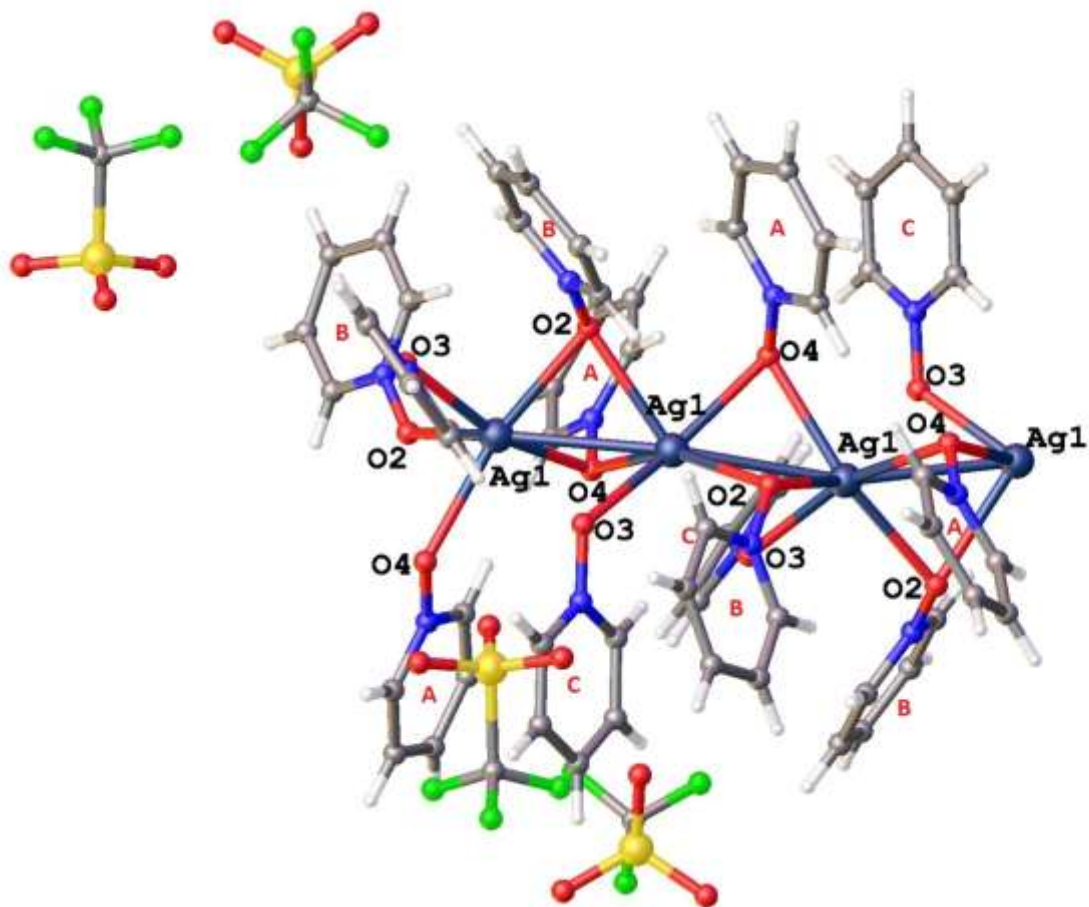


Figure S5: View of the crystal structure of [Ag(py-O)₃][OTf] showing the Ag...Ag interactions and bridging py-O ligands.

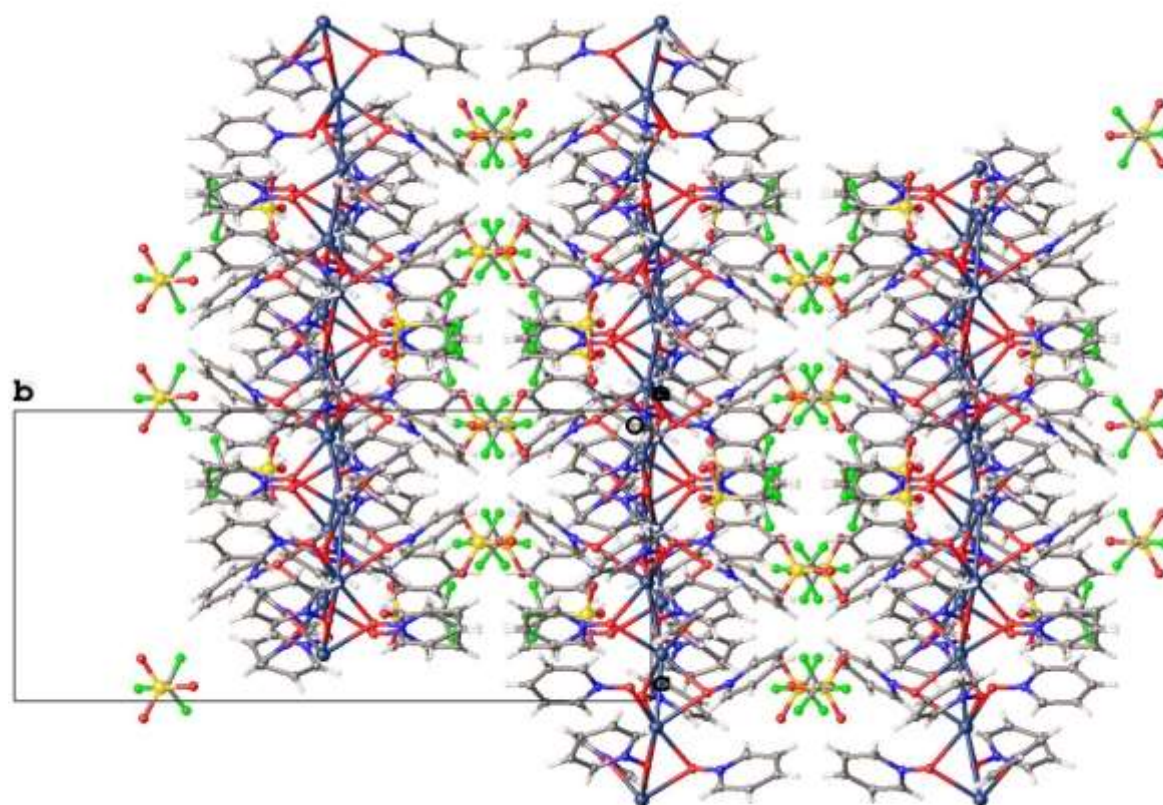


Figure S6: View of the packing of the $[\text{Ag}(\text{py-O})_3]_\infty$ moieties and anions in the structure of $[\text{Ag}(\text{py-O})_3][\text{OTf}]$.

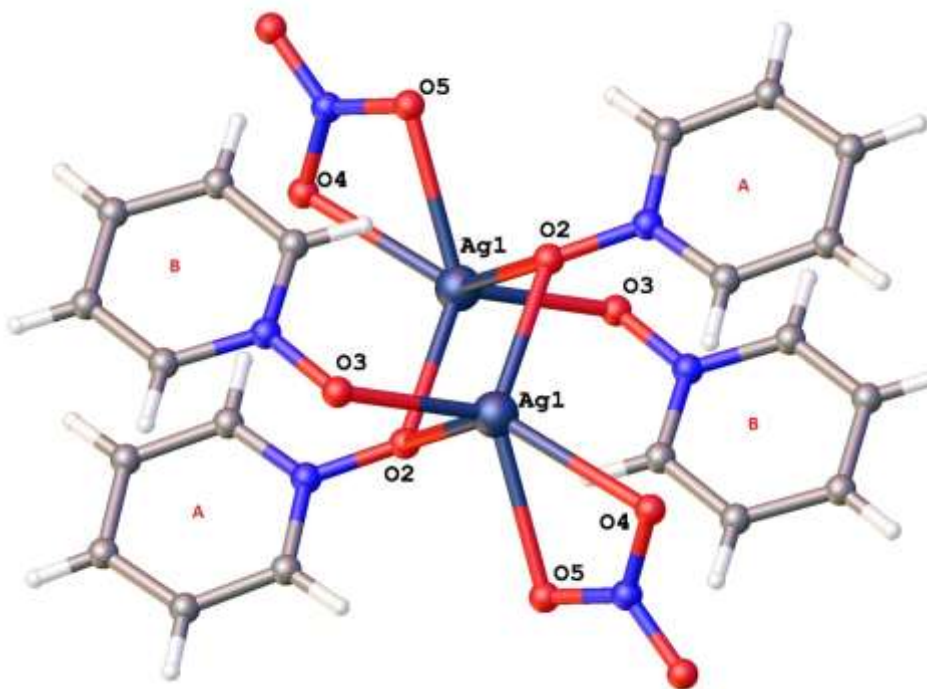


Figure S7: View of the crystal structure of [Ag(py-O)₂][NO₃] showing dimeric [Ag₂(py-O)₄(NO₃)₂] moiety formed.

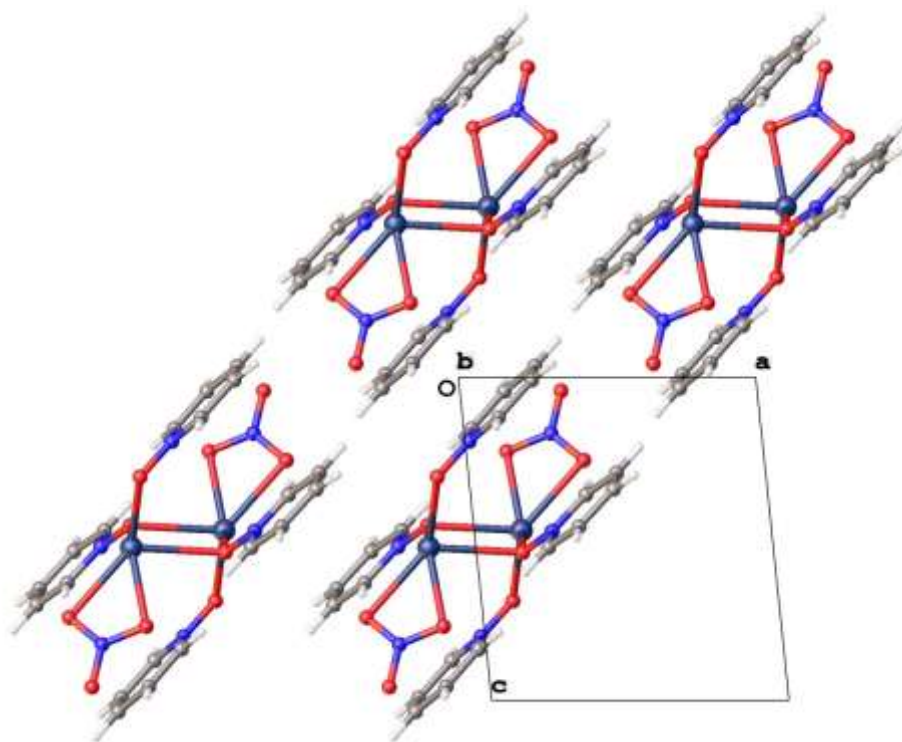


Figure S8: View of the packing in the crystal structure of [Ag(py-O)₂][NO₃].

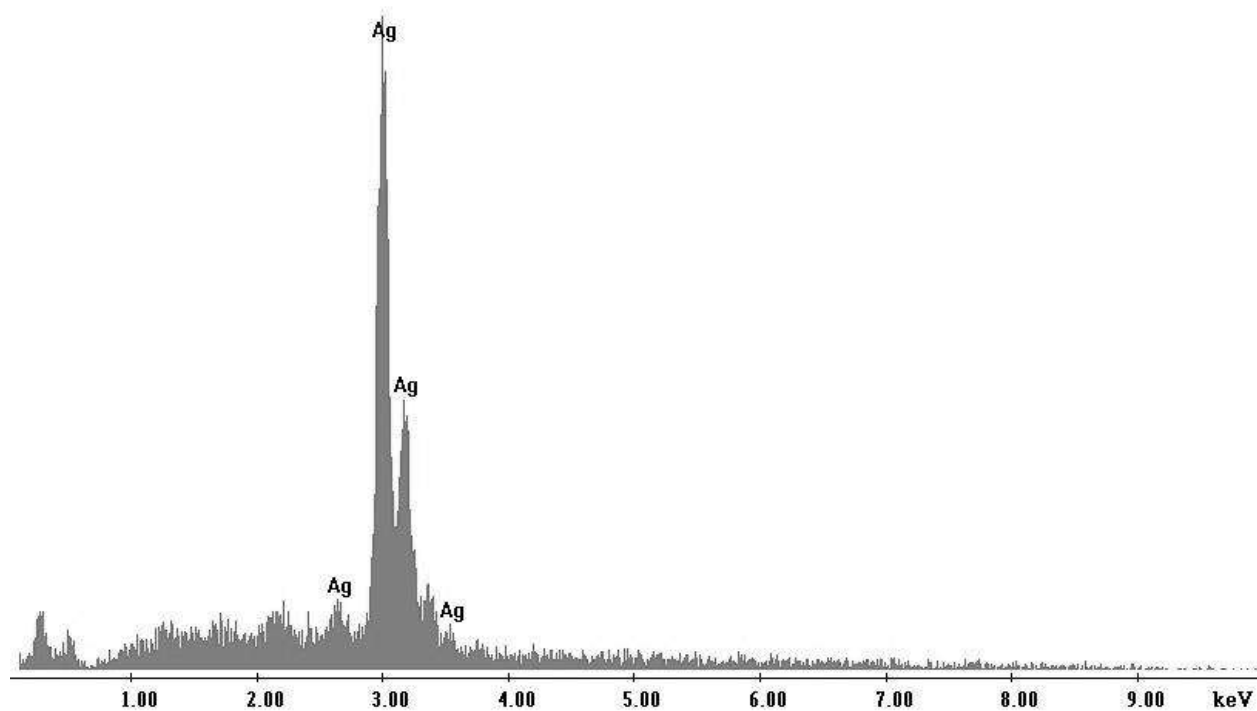


Figure S9: EDX spectrum of a silver deposit of $[\text{Ag}(\text{pyO})_3][\text{NO}_3]$ plated at -1.0 A dm^{-2} for 60 seconds at 90°C showing only peaks of silver, indicating that the gold substrate is completely covered and the deposits are pure silver.